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Short communication

Paired electrolysis for simultaneous electrochemical water softening and production of weak acid solutions

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ABSTRACT

In this work, a new paired electrolysis procedure is successfully introduced. This is a combination of two different processes: electrochemical water softening (EWS) and electrochemical production of weak acid solutions (EPWA). This paired electrolysis method is tested for hardness removal in a simulated solution of concentrates, such as that produced by the electrodialysis of brackish water. The use of a divided electrochemical cell makes it possible to achieve removal efficiencies higher than 90% in optimum conditions. The good performance and stability of the cathode are also demonstrated by long-term experiments. Simultaneously, weak acids are obtained by protonation of their conjugate bases in the anodic compartment. Lactic acid is obtained from lactate with a purity of no less than 80% in this work without significant loss of efficiency in hardness removal. The main interest lies in the commercial value of weak acids such as lactic acid, citric acid or gluconic acid, among others. The methodology makes it possible to benefit from both cathodic and anodic processes, which may contribute to decreasing the final EWS treatment costs for a cost-effective desalination application.

1. Introduction

Fresh water is becoming scarce due to human activities [1,2]. Many regions need to resort to groundwater [3] but in many cases this is contaminated with saline [4–6]. Electrodialysis is a membrane-based technology for brackish water desalination [7–10], which could be a solution to this problem. However, its application is limited by the generation of a concentrate that has to be properly managed [11,12]. One possible solution would be to decrease the volume of concentrate, but this is difficult because concentrates usually contain high concentrations of Ca^{2+}, Mg^{2+}, SO_4^{2-} and HCO_3^- ions and this would cause scaling problems in pipelines.

A number of methods are available for controlling water hardness [11,13–18], including pH control, chemically-induced precipitation, crystallization inhibitors and ion-exchange resins. The main drawbacks of these methods are the addition of chemicals, the increase in electrical conductivity and the management of wastes. Electrochemical water softening (EWS) is an interesting alternative [19–21]. The basic principle of EWS is to use water electrolysis to achieve a high concentration of hydroxide ions in the vicinity of the cathode, forcing the precipitation of the insoluble compounds onto its surface. EWS has the usual advantages of electrochemical techniques: simple maintenance, eco-friendliness and convenient process control [22]. Nevertheless, it also has some technical limitations preventing its use, such as the requirement for a large electrode area [23]. New approaches have been found in literature to overcome the problems: scale detachment processes [24], $CaCO_3$ seeds [25], coupling with electrocoagulation [26], use of 3D cathodes [27], and the separation of anodic and cathodic compartments by a cation-exchange membrane [28–30]. The last achieves the highest removal efficiencies reported. Using a divided electrochemical cell (Fig. 1), OH^- ions generated on the cathode are not neutralised by H^+ generated on the anode and finally a high pH value is reached in the whole catholyte at the steady state, resulting in a higher efficiency compared to the undivided cell configuration [31]. The anolytes are usually NaCl or Na_2SO_4 solutions, which are acidified during the process. Despite having a high efficiency, the technique is not yet sufficiently cost-effective for practical applications.

In this paper, a divided EWS cell is tested using a simulated version of the concentrates produced by groundwater desalination through electrodialysis. A new methodology based on two coupled electrode processes is proposed: EWS is performed at the cathode and a weak acid solution is produced (EPWA) at the anode. The latter is generated by protonation of the corresponding conjugate base (Fig. 1). This methodology has several advantages: (I) The anolyte can be used for longer because acidification occurs more slowly (compared to NaCl or Na_2SO_4). (II) The crossover of H^+ through the cation membrane

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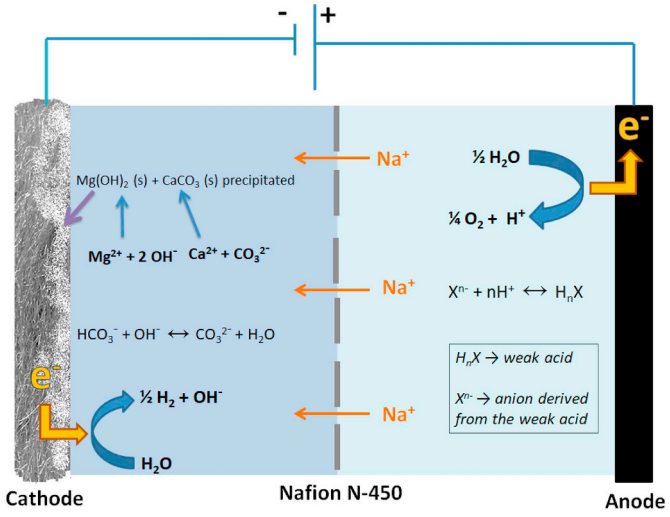

Fig. 1. Scheme for the paired electrolysis process EWS + EPWA.

(efficiency loss) is hindered. (III) The weak acid solution can be recovered with a suitable purity and valorised. The main interest lies in the commercial value of weak acids [32] (lactic acid, gluconic acid, citric acid, formic acid, etc.). Solutions of conjugate bases are usually obtained from carbohydrate fermentation processes [32–34]. Salts are produced instead of the corresponding acids because these processes require a neutral pH to maintain a high-growth environment for bacteria and, therefore, the subsequent transformation into the acid form is necessary. The proposed EWS + EWAP methodology can transform salts into their corresponding weak acids while simultaneously eliminating hardness from water. Thus, the same electrical energy is used for two valuable processes. In this work, two different acid–base systems are evaluated: the orthophosphoric acid species and the lactate–lactic acid pair. The orthophosphoric system is chosen because it can be used for longer with a lower concentration, since it involves a triprotic acid, and the lactic system because of the commercial value of the lactic acid. The goal of this work is to propose a methodology that would reduce the EWS costs by making money from the anodic process. This would make the technology more cost-effective for applications in desalination.

2. Materials and methods

2.1. Chemicals and solutions

Detailed information about chemicals is given in a previous work [27]. Additionally, as anolytes: (+)-lactic acid [HLa, (Panreac 85%)] and anhydrous sodium orthophosphate [Na_3PO_4, (AlphaAesar 99%)] were used. Table 1 presents the composition of the catholyte, whose preparation is described in reference [27]. Anolytes were prepared at different concentrations (Na_3PO_4: 0.1 M and HLa: 0.1, 0.25 and 1 M). NaLa solutions were obtained by adding NaOH (Scharlau 99%) to HLa solutions until pH 8.0 was obtained.

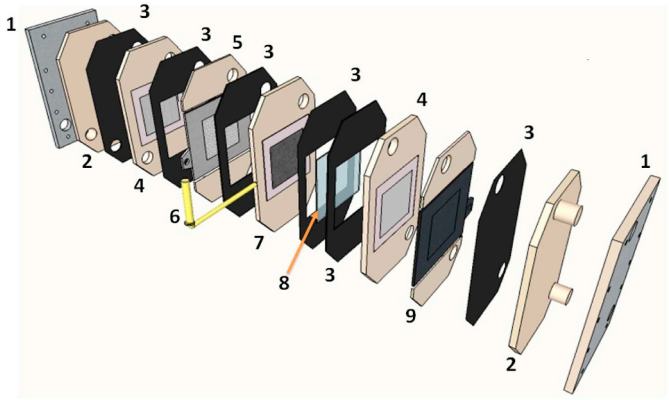

Fig. 2. Filter-press reactor scheme. 1) End plates. 2) Plastic frames. 3) Rubber sealings. 4) Flow frame sets. 5) Ti mesh between two spacers. 6) Reference electrode AgCl/Ag (3.5 M KCl) 7) *3DSSW* set in the inner space of a flow frame set. 8) Cation-exchange membrane. 9) *DSA*-O_2 anode between two spacers. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2.2. Electrolytic system

Fig. 2 shows the design of the divided filter-press electrochemical reactor (ElectroMP-Cell, ElectroCell). Cathodic and anodic compartments were separated by a Nafion N-450 (Dupont, USA) cation-exchange membrane. The anode was a 100 cm^2 oxygen evolution DSA (IrO_2 film on a Ti plate). The 3D cathode was stainless steel wool (AISI 434) with a Ti mesh as current collector. A flow-through configuration was used. The weight of the SS wool used was always around 6 g (10 cm height × 10 cm length × 1.25 cm width). The inter-electrode distance was 1.35 cm.

The cell was operated in galvanostatic mode at a current density (j) interval between 25 and 200 A m^{-2} (Elektro Automatik MODEL EA-PS 2032–050 DC). The catholyte was circulated in continuous mode at flow rates (Q) in the range 0.2–2.7 L h^{-1} (ISMATEC REGLO digital). The working ranges were selected according to the literature [19,25]. The anolyte was recirculated in batch mode at 10.4 L h^{-1} (Heidolph PumpDrive 5206).

2.3. Instruments and analytical procedures

Water hardness (mg L^{-1} $CaCO_3$) was measured by EDTA titration (702 SM Titrino [Metrohm]) [35]. Ca^{2+}, Mg^{2+} and Na^+ were measured by inductively coupled plasma mass spectroscopy (ICP-MS, Thermo Elemental, VG PQ Excell). The weak acid concentration in the anolyte was determined by Na^+ analysis and pH measurement (Crison Micro pH 2000 pH-meter). All samples were filtered with a 0.45 µm pore nylon filter before the analysis and measured twice.

2.4. Performance data

Specific energy consumption (EC) and hardness conversion (C, %) are used to determine efficiency:

Table 1
Chemical parameters of the synthetic cathodic feed water.

Parameter	pH	Conductivity/mS cm^{-1}	Hardness/mg L^{-1} $CaCO_3$	Alkalinity/mg L^{-1} $CaCO_3$
Value	7.4	5.03	2350	1400

Chemical composition							
Component	Mg^{2+}	SO_4^{2-}	Ca^{2+}	Cl^-	NO_3^-	Na^+	HCO_3^-
Concentration/mg L^{-1}	200	770	600	1000	800	400	850

$$C = \frac{H_o - H_f}{H_o} \cdot 100 \quad (1)$$

where H_o is the original hardness and H_f is the steady-state value of final hardness, both in mg L^{-1} $CaCO_3$.

$$EC_{EWS} = \frac{V_{cell} \cdot I \cdot t}{m_{CaCO3}} \cdot 10^{-3} \quad (2)$$

$$EC_{EWS+EPWA} = \frac{V_{cell} \cdot I \cdot t}{m_{CaCO3} + m_{acid}} \cdot 10^{-3} \quad (3)$$

where V_{cell} is the average cell voltage (volts), I is the current intensity (amperes), t is the experiment time (hours), m_{CaCO3} is the mass of insoluble compounds removed (kg) and m_{acid} is the mass of weak acid obtained (kg). $EC_{EWS+EPWA}$ introduces the concept of the valorization of organic weak acids lowering the final cost of the process.

The purity of the acid (%) is defined as the ratio acid/conjugated base for a given concentration.

3. Results and discussion

3.1. Paired EWS + EPWA experiments

Different experiments were initially conducted to find the optimum values of j and Q, within the ranges mentioned in Section 2.2. The values showing the best relationship C-EC were j: 100 A m^{-2} and Q: 1.2 L h^{-1}, with an EC_{EWS} of 2.78 kWh kg^{-1} $CaCO_3$, 90%–95% efficiency and a final pH value of 10.6 (catholyte). The anolyte was always Na_3PO_4 0.1 M (2 L). Table 1 presents the composition of the catholyte solution for all the experiments described in this section.

Table 2 shows the results (final catholyte pH, V_{cell}, C, acid purity and EC) for experiments carried out under different conditions for comparative purposes and several conclusions can be drawn. Experiment 1 refers to an EWS experiment with a single-cell configuration from a previous work [27]. Experiment 2 is a paired electrolysis with the orthophosphoric acid (0.1 M) system whereas Experiments 3 and 4 use the lactic acid system (0.1 M). Experiment 3 reaches a weak acid purity of 83% of without C loss while Experiment 4 reaches a high 95% purity with a loss of 30–40 percentage points of C. Clearly, the divided cell configuration achieves higher efficiencies in terms of hardness removal (about 45% points) and lower EC values. The differences in terms of EC between the divided and the undivided configuration are not large, but it should be considered that, as the purity of the weak acid is increased, the electrical conductivity of the anolyte decreases. The higher inter-electrode distance and the membrane must be also considered for the divided cell configuration. However, the divided experiments allow us to obtain valuable solutions of weak acids. Without any decrease in C (90–95%), the H_3PO_4 purity can be about 50% (Exp. 2) whereas the HLa purity can reach approximately 83% (Exp. 3). Additionally, the HLa solutions have more commercial value than the H_3PO_4 ones and for this reason the $EC_{EWS+EPWA}$ concept is introduced (involves an organic weak acid) and distinguished from EC_{EWS}. When analyzing the EC values, it should be taken into account that a 0.1 M NaLa solution is less electrically conductive than a 0.1 M Na_3PO_4 solution. HLa purities up to 95% can be reached but this compromises the value of C, which decreases to around 70–80%, and EC, which increases.

Fig. 3(a–d) show the plots of C and weak acid purity versus time for experiments with anolytes of different compositions and concentrations: Na_3PO_4 (0.1 M) and NaLa (0.1, 0.25 and 1 M). It can be observed that before C drops under 90%, the H_3PO_4 purity reaches 50% while the HLa purity reaches approximately 80% in all cases. The behaviour of the acids (triprotic versus monoprotic) is different because a polyprotic acid needs to undergo multiple protonation processes. The figure also shows that HLa purities up to 95% can be reached with values of C within the range 70–80%. The results show that at pH values under the first pKa of the conjugated acid–base pair, H^+ starts to cross the membrane towards the catholyte, decreasing the C value. Ca and Mg concentrations in the anolyte were always under 20 ppm, meaning that these divalent cations do not cross the membrane in significant amounts. Also, it is interesting to note that the ability of the electrochemical reactor to carry out the EWS with high values of hardness conversion will depend on the initial concentration of the conjugate base and the volume of anolyte.

3.2. Long-term experiments

Long-term experiments were performed using Na_3PO_4 0.1 M (25 L) as anolyte. The hardness conversion, C, remained stable at around 90% throughout the experiment. Anolyte pH values were also stable in the range 10.5–11. V_{cell} remained within the range 4.5–5 V throughout the experiment. The system collapsed after approximately 35 h. It is important to note that V_{cell} and C did not vary during the experiment, which means that the cathode was not significantly blocked by precipitation of insoluble compounds and was working correctly up to this point. Once the electrochemical cell had been disabled and checked, it was found that the operating problem was that the outlet of the catholyte flow-frame set had been plugged by precipitates. As described earlier, when the EWS is carried out in a divided cell the pH of the treated catholyte is around 10.5, and the precipitation of insoluble compounds also takes place in the bulk of the solution and not only on the cathode surface. The filter-press reactor used in this work as a proof of concept is not the optimum design for this kind of process. This issue should be addressed with further work on the reactor design.

4. Conclusions

In this work, a new methodology based on paired electrolysis is successfully introduced and tested. The process consists in simultaneously carrying out the electrochemical softening of water (EWS) and the electrochemical production of a weak acid solution (EPWA) of commercial interest. The EWS + EPWA process was tested for hardness removal in simulated ED concentrates from brackish water desalination. The divided cell configuration showed excellent efficiencies, much higher than for the undivided systems, with C above 90% under optimum conditions (j = 100 A m^{-2}, Q = 1.2 L h^{-1}). Long-term experiments showed that the cathode was stable for 35 h and the failure of the system was attributed to the reactor design. Simultaneously, H_3PO_4 and HLa are obtained with purities of 50% and 83%, respectively, without significant loss of efficiency in C. Purities up to 95% are achievable for HLa with a decrease in C not higher than 10–20 percentage points. Since weak acids like lactic acid can be valorised due to their commercial value, this methodology may help lower the final treatment

Table 2
Experimental data for EWS experiments and calculated energy consumption.

Exp.	V_{cell}/V	pH cat	C/%	Acid purity/%	EC_{EWS}/kWh kg^{-1}	$EC_{EWS+EPWA}$/kWh kg^{-1}
1	3.90	5.5	35–45	–	3.48	–
2	7.20	10.6	90–95	50 (NaOH)	2.78	–
3	7.72	10.8	90–95	83 (HLa)	2.97	0.85
4	10.95	7.62	70–80	95 (HLa)	7.06	2.17

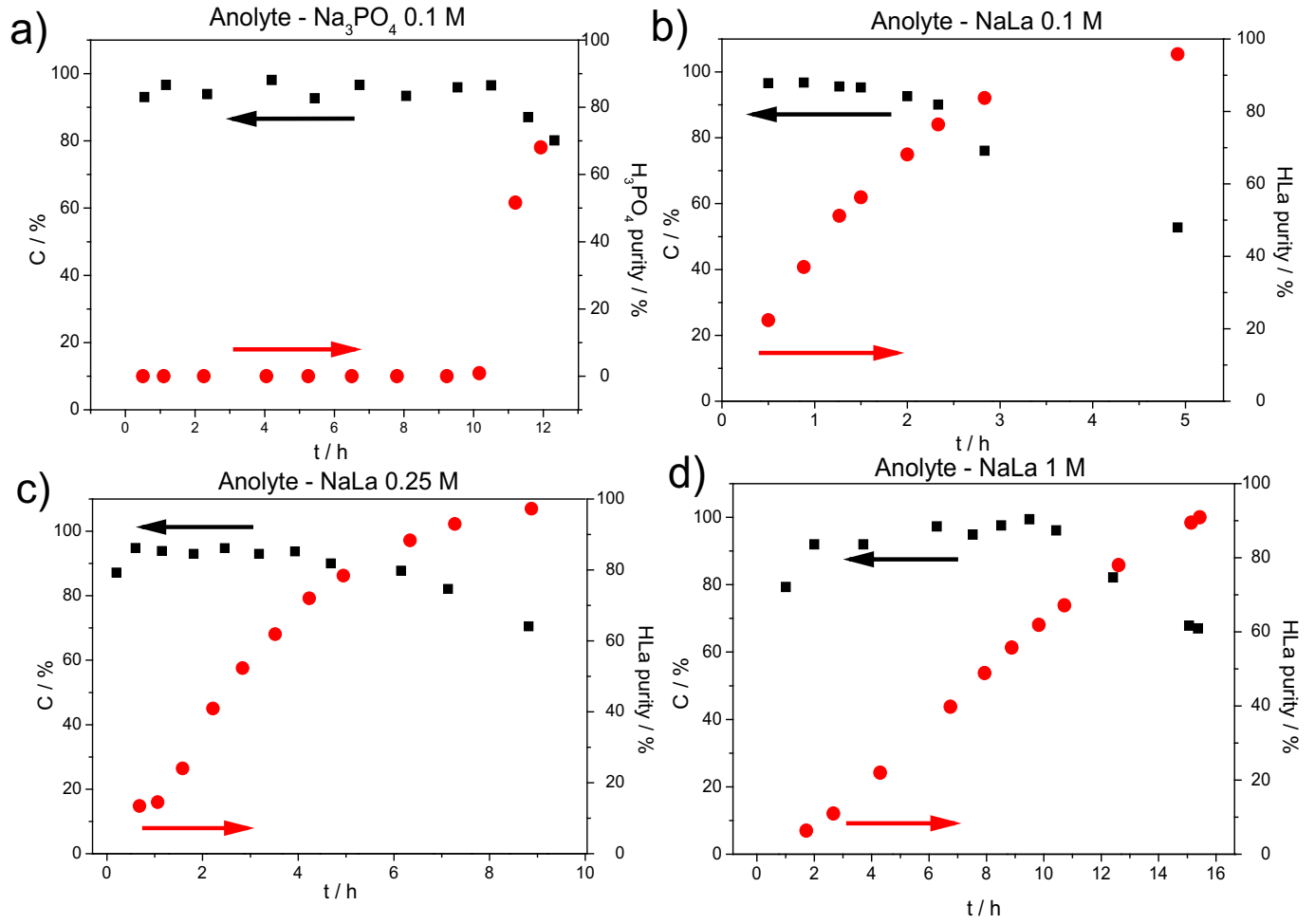

Fig. 3. EWS + EPWA experiments at different experimental conditions. Plots of *C* (black squares) and weak acid purity (red circles) versus time: a) Na_3PO_4 0.1 M b) NaLa 0.1 M c) NaLa 0.25 M and d) NaLa 1 M. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

cost and make the technique cost-effective for use in desalination. Further investigations are needed to assess the best working conditions such as the reactor design.

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